

# PATENT ABSTRACTS OF JAPAN

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(54) TREATMENT METHOD FOR PREVENTING ELUTION OF LEAD FROM LEAD-CONTAINING COPPER ALLOY

(57)Abstract:

**PROBLEM TO BE SOLVED:** To provide a method for preventing such a phenomenon that lead elutes from a metal piece for water supply pipe of a water feed apparatus made of a lead-containing copper alloy material into the water in use.

**SOLUTION:** In the method for preventing the elution of lead into water, as pretreatment, the surface of a metal piece for water feed made of a lead- containing copper alloy material is cleaned with an alkaline degreasing solution containing caustic soda and a surfactant. After being plated by an ordinary nickel-chromium plating process, the metal piece is dipped into a chromium- containing chromate treatment solution containing an aromatic heterocyclic compound such as benzotriazole, or an aqueous solution of phosphoric acid and phosphate, or an acidic solution, or an alkaline solution, or a neutral solution so that a firm film is deposited on the surface.

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CLAIMS

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[Claim(s)]

[Claim 1]In order to remove a surface oil film and others by considering metal parts made from a lead content copper alloy (many are used for a waterworks appliance implement of a boiler feeding device) as washing processing, Elution preventive means of lead by carrying out dipping treatment to a solution having contained aromatic heterocyclic compounds [, such as benzothiazole and its salt, ], such as benzotriazol and benzotriazol system various compounds, after defecating the surface by immersion of a caustic alkali system degreaser or electrolytic treatment [Claim 2]

[Claim 1]in -- benzotriazol, benzotriazol system various compounds, etc. for a product after nickel and chrome plating, And elution preventive means of lead by carrying out dipping treatment to acidity, alkalinity, or neutral liquid having contained aromatic heterocyclic compounds, such as aromatic heterocyclic compounds, such as various compounds, such as benzothiazole and its salt

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[Translation done.]

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to the elution preventive means of lead from the parts made from the lead content copper alloy for preventing lead from being eluted into tap water from parts, such as rinsing metal fittings made from a lead content copper alloy.

[0002]

[Description of the Prior Art]The \*\*\*\*\* public-funds implement is manufactured through processes, such as cutting, in copper alloy casting or the copper alloy bar, and the tubing material, it is the purpose of the processability enhancement at the time of this cutting, and lead of several percent (example; BC-six about 5%, 2 to 3% of free cutting brass) is usually added by these copper alloys.

[0003]The lead added by the copper alloy does not form the solid solution called a mix crystal like a general alloy, and compounds, such as an oxide of lead and lead, distribute granular, and it exists, and it is said that it gathers on the surface of an alloy in the case of a casting. It is thought that this phenomenon is based on specific gravity difference.

[0004]Elution of lead from the hydrant of a waterworks recently came [ therefore, / by letting water pass to this from the \*\*\*\*\* public-funds implement manufactured with the lead content copper alloy, / elution of underwater lead was not avoided, but the concern to which this has an adverse effect on a human body was assumed, and ] to be regarded as questionable.

[0005]However, cutting is difficult for the copper alloy material by which lead is not added, it is not suitable for what processing of the details like faucet metal fitting requires, and the lead content copper alloy material which has in addition [ now ] good machinability is used.

[0006]Although there is also a method which immerses the parts made from a lead content copper alloy in strong-base liquid for these solutions, carries out a slight etching process, and is eluted in lead and the plumbic acid ghost near the alloy surface, now, it is difficult to prevent leaden elution thoroughly.

[0007]

[Problem(s) to be Solved by the Invention]This invention immerses the product feed water public-funds implement made from a copper alloy containing lead with good processability in a treating solution, a firm coat is made to form in the copper alloy surface, and how lead prevents being underwater eluted at the time of feed water is provided.

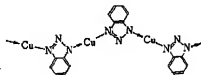
[0008]

[Means for Solving the Problem] An alkaline degreaser etc. wash this invention by considering a feed water public-funds implement made from a lead content copper alloy as pretreatment, an acidic solution which does not contain a chromium compound having contained aromatic heterocyclic compounds, such as aromatic heterocyclic compounds [ , such as benzothiazole and its salt, ], such as benzotriazol system various compounds, or a chromium compound after plating with the usual plating process -- or -- the same -- alkaline liquid -- or it being immersed in neutral liquid similarly and, A firm coat is made to form in the copper alloy surface, and leaden elution is prevented.

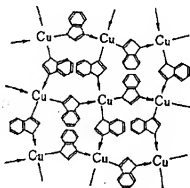
[0009]

[Consideration until it results in this invention] Many organic compounds which may combine with copper, may form a coat and may protect the surface exist until it results in a benzene derivative which contains nitrogen or sulfur from a long-chain aliphatic series sulfide.

[0010] Although phthalocyanine copper is famous for a heterocyclic compound which nitrogen which has an unshared electron pair, and copper combine, benzotriazol is one of those which form a firm coat easily invaded by neither water nor solvent, and are excellent in adhesion. As for structure of the coat, the structure is clarified as follows by Cotton and J.B.\*



a) In the case of cuprous salt



b) In the case of cupric salt

\*) Proc. 2nd Inter. Cong. on  
Metallic Corrosion, P. 590,  
NACE, N. Y (1966).

[0011] Usually, since copper is the second copper when it is in the atmosphere, like b, it becomes mesh shape, and joins together, therefore it is thought that a firm coat is formed.

[0012] An artificer made a coat with a compound of copper and benzotriazol form by being immersed in a treating solution which contains benzotriazol paying attention to this point, and it thought of preventing leaden elution.

[0013] 2-mercaptobenzimidazole, 1-hydronaliumbenzimidazole, benzimidazole, guanine, adenine, etc. are one of structure of benzotriazol, and comparatively similar things, Although it is accepted that these compounds also form a compound of copper and nitrogen which has an unshared electron pair, since the coat is not so firm as benzotriazol, leaden elution is accepted slightly. Although there are 2-mel helmet benzothiazole ( $C_7H_5NS_2$ ) and its salt other than the above-mentioned analogue, This reacting to copper like benzotriazol and forming a firm protective film is known, it met in flat knot, and it was checked by experiment that it is dramatically effective in prevention from lead elution. However, it is poorly soluble at water, this substance is

weak to oxidizing acid, such as chromic acid and sulfuric acid, and since it is selected by target substance as a carcinogen to \*\*\*\*, it is not practical.

[0014]Combination with benzotriazol and copper is quite firm, and it is known by packing copper ware on rustproof paper experientially impregnated with benzotriazol about 2% that it will be useful for rust prevention of copper for a long period of time.

[0015]If an electrical part which consists of an alloy of \*\*\*\* is processed with a steam of benzotriazol, it also turns out that contact resistance does not change over a long period of time.

[0016]It was guessed that it formed a coat by a reaction with copper even if liquid in which an artificer contains benzotriazol from these facts is acidity, alkalinity, or neutrality. What made various solution in which acidity or alkalinity which actually contains benzotriazol differs, and carried out dipping treatment of the lead content copper alloy discovered that a grade of leaden elution had a big difference as compared with what is not contained.

[0017]Although metalead anticorrosion has an approach which makes a corrosion-resistant outstanding coat from before by chromate treatment, many this is used as anticorrosive processing of zinc, post-processing of a cadmium plate or aluminum, and its alloy. With copper or other alloys, although generation of that protective film is weak, it is supposed that there are some effects this chromate treatment in brass.

[0018]Then, chromate treatment is performed to a lead content copper alloy, and although existence of leaden elution was investigated, as compared with an unsettled thing, a lead elution volume becomes quite small.

[0019]If benzotriazol is added in this chromate liquid, most leaden elution will be lost.

[0020]That is, a direction of a chemical film which changes from a mixed coat of copper, benzotriazol or benzotriazol, and chromium to prevention from lead elution from a coat of chromium is the proof which is a far firm coat.

[0021]Next, although it was attached to three compounds with a structure similar to benzotriazol of guanine, benzimidazole, and adenine, and it investigated, and a lead elution preventive effect was seen by each, as for neither, an effect like benzotriazol was accepted.

[0022]When 2-mercaptobenzothiazole and its salt were added and investigated in chromate liquid of chromic acid content, a remarkable effect was seen, but it turned out that liquid changed brown and decomposition has taken place clearly. Change in which concomitant use with a commercial chromate agent for zinc and mixing are also the same as for this was checked. This has a tendency with the same said of benzotriazol -- mixing with a high-concentration chromic anhydride, or a previous process of chromic acid -- pouring in -- since oxidative degradation is brought forward, it is necessary to consider it as necessary minimum As for the criteria of control, according to the experiment, it is desirable to consider it as about 10 g/l or less.

[0023]Now, an effect is seen, even if prevention from elution of lead has an effect since the acidity or alkalinity of a solution which contains benzotriazol as mentioned above forms copper and a chemical film also by acidity, alkalinity, and also neutrality, and alkali and neutral substances are added to an acidic solution, it is considered as an acidic solution and it uses together.

[0024]If attached to acidity, decomposition of benzotriazol has an effect of chromic acid with the concentration, but an effect of prevention from coat formation lead elution is accepted notably, and although sulfuric acid and chloride are also effective, it is inferior to chromic acid.

[0025]Acid which has acid, chloride, and a chloride group which have acid, sulfuric acid, and a sulfuric acid group which have phosphoric acid and a phosphate group as an acidic solution, and glycolic acid and organic

acid (for example, oxalic acid, citrate, malic acid, etc.) are also effective.

[0026]As alkaline liquid, an effect can see strong basicity acid, phosphate, carbonate, silicate, etc. As neutral liquid, various neutral salt, a solvent of benzotriazol, and its combination are also considered.

[0027]Next, although it is phosphoric acid, phosphoric acid has few risks of invading metal unlike sulfuric acid and chloride, therefore it is comparatively safe [ phosphoric acid ] even if concentration is high. According to the reconnaissance examination, even if there are few effects, prevention from elution of lead has a big effect in liquid which added benzotriazol at not less than 50 g/l and it compares this with chromic acid by concentration of 10 g/l, there are few leaden elution volumes far.

[0028]Considering corrosion by acid of a raw material, in the case of an acidic solution, concentration is limited itself, but in the case of phosphoric acid, even if it is about 100-150 g/l in concentration, there is little influence on a raw material. Temperature will become firm [ a reaction ] early again, if it warms, but it is enough in 5 minutes at ordinary temperature.

[0029]When chromic acid is used, there is not necessarily elution of chromium, and also future still severer regulation can be considered from a viewpoint on a public nuisance and safety and hygiene, but phosphoric acid has few such problems.

[0030]In an alkaline case, a coat by benzotriazol is formed, but since it is weak compared with acidity, there are many leaden elution volumes.

[0031]Although a result a little better than alkalinity was obtained neutrally, there are more leaden elution volumes than a case of mist [ this ] beam acidity.

[0032]This reason is considered with acidity to be because for a surface of metal to be activated with acid.

[0033]Next, although an example explains this invention concretely, this invention is not limited at all by this example.

[0034]

[Example-1] The following lead content copper alloy was used for an example. JIS H3250 (C3604) free-cutting-brass round bar cutting article (Cu:57.0-61.0, Pb:1.8-3.7, less than Fe:0.5, less than Sn:0.7, Zn: remainder and unit %)

[0035]A treating solution used solution of the following presentation.

A: 30 g/l of bichromate of soda, 6 g/l of sulfuric acid, 6 g/l of benzotriazol 5 g/l/B:sulfuric acid, 50 g/l of benzotriazol 5 g/l/C:phosphoric acid, benzotriazol 5 g/l/D : 50 g/l of phosphoric acid, benzotriazol 10g/l/E: 100 g/l of phosphoric acid, benzotriazol 10 g/l/F: Sodium hydroxide 2.5 g/l, benzotriazol 5 g/l/G:ethyl alcohol 15 g/l, 5 g/l of benzotriazol [0036]test sample construction material; -- free-cutting-brass C3604BD and faucet-metal-fitting

part; -- about 33 g and surface area;44.0-cm<sup>2</sup>[0037]Lead elution prevention examination-1 sample is immersed in alkaline degreaser solution (50 g/l) containing caustic alkali of sodium, a surface-active agent, etc. for 10 minutes at 50 \*\*, the oil and fat which adhered on the surface of a sample, and others are removed, and a specimen surface is defecated. Rinsing desiccation was carried out after this was immersed in above-mentioned treating solution A-G for 2 minutes at 50 \*\*.

[0038]The lead elution test of the sample which carried out dipping treatment with the treating solution of lead elution test-1 A-G was done, and the effect was judged. The unsettled sample (only degreasing treatment) also performed lead elution for comparison.

[0039]Since it was eluted for leaden elution for a short time, 0.01% of acetic acid solution was used as an accelerated test. The elution conditions are as follows. 0.01% of acetic acid solution: 200 ml, a

temperature:room temperature, immersion time:5 minutes [0040]By lead elution test result-1 above-mentioned treating solution A-G, the sample in which lead carried out the elution preventing process was immersed in 0.01% of acetic acid solutions [ 200 ml of ] for 5 minutes at the room temperature, and the eluted lead was measured.

表 1

	鉛溶出防止処理条件		0.01%の酢酸溶液中に 浸出した鉛量 (ppb)	試料1cm当りの鉛量 (μg)
	温 度	時 間 (分)		
未処理	25℃	5	2150	9.77
処理液A	〃	〃	27	0.12
処理液B	〃	〃	65	0.30
処理液C	〃	〃	25	0.11
処理液D	〃	〃	11	0.05
処理液E	〃	〃	12	0.05
処理液F	〃	〃	250	1.14
処理液G	〃	〃	180	0.82

[0041]If the result processed by treating solution A-G is seen, as compared with what has unsettled all, the leaden elution volume will decrease substantially.

[0042]When these results are compared, A has a remarkable effect, but it is less than DE. The elution volume of \*\*\*\* is considered for the phosphoric acid concentration of not less than 50 g/l and the treating solution of about 10 g/l of benzotriazol to be practical with regards to the concentration of phosphoric acid and benzotriazol, in view of this example.

[0043]Since the use as an object for common water supply system water was most, that lead elution test-2 feed-water metal-fittings parts are actually used did the lead elution test by city tap water.

[0044]The lead which immersed the sample in which lead carried out the elution preventing process in 200 ml of Nagoya tap water, and was eluted by lead elution test result-2 above-mentioned treating solution A-G was measured.

表 2

	鉛溶出防止処理条件		名古屋水道水中に 浸出した鉛量 (ppb)	試料1cm当りの鉛量 (μg)
	温 度	時 間 (分)		
未処理	25℃	48	180	0.81
処理液A	〃	〃	検出せず	—
処理液B	〃	〃	〃	—
処理液C	〃	〃	〃	—
処理液D	〃	〃	〃	—
処理液E	〃	〃	〃	—
処理液F	〃	〃	25	0.11
処理液G	〃	〃	20	0.09

As compared with 0.01% of acetic acid solution, there were very few leaden elution volumes and lead was not able to be detected from the sample processed about A-E.

[0045]

[Example-2] With the content \*\*\*\* treating solution, the effect remarkable to the prevention from elution of lead was seen in benzotriazol. Now, about three sorts in the above-mentioned compound with which benzotriazol and chemical structure were next similar, the acid aqueous solution is used as a treating solution, and it compares with example-1. The used compounds are three compounds of guanine, benzimidazole, and adenine. Although such structures are similar with benzotriazol, it is a diazole compound altogether.

[0046]

[Example-3] The test sample used the same thing as Example 1.

[0047]The treating solution used the solution of the following presentation.

H: 6-g/l and 10 g/l of sulfuric acid guanine I:sulfuric acid 6 g/l, 10 g/l of benzimidazole J : sulfuric acid 6 g/l, 10 g/l of adenine [0048]Pretreatment of lead elution preventing process-2 sample was performed like lead elution preventing process-1. This was immersed in above-mentioned treating solution H-J for 2 minutes at 50 \*\*, and rinsing desiccation was carried out.

[0049]The sample which carried out the lead elution preventing process with the treating solution of lead elution test-3 H-J was immersed in 0.01% of acetic acid solution like example-1, and the leaden elution volume was measured.

表 3

	鉛除去防止処理条件		0.01%の酢酸水溶液中に	試料1.0g当りの溶出
	温度	時間 (分)	溶出した鉛量 (ppb)	鉛量 (ppb)
処理液 H	25℃	5	220	1.01
処理液 I	〃	〃	105	0.89
処理液 J	〃	〃	200	0.92

[0050]Lead elution test result-3

[0051]Although there are quite many leaden elution volumes as compared with the benzotriazol of Example 1, as compared with the unsettled sample, reduction is carried out to the 1/10th place. It seems that a film strength with copper is weak compared with benzotriazol, or this is because a coat dissolves in water. That is, in diazole, a firm coat like triazole is imagined to be what is not made easily. However, if it presumes from elution test result-2 of the point when this is immersed in tap water, it will be thought that the quantity eluted in tap water is set to about 20-25 ppb on the conditions.

[Translation done.]